

AN EXTENSION OF THE THALLIUM II SPECTRUM

By

CECIL B. ELLIS

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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CECIL B. ELLIS, *University of Michigan*

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The spectrum of thallium from the hollow cathode discharge in He has been photographed in the region from 9250Å to 600Å. The classification of the first spark spectrum has been approximately doubled by the assignment of 160 new lines, which locate 35 new levels. These include members up to $n=11$ and 12 of the s , p , and d series (which establish the ionization potential as $164,765 \pm 5 \text{ cm}^{-1}$), the

first two members of the g series, and six levels of the $5d^96s^26p$ configuration. Perturbations are present in many of the series, due to their interaction with the $6p^2$ and $5d^96s^26p$ configurations. The $6s6g$ term appears to have hyperfine structure larger than its multiplet structure. Practically all of the hollow cathode lines of thallium in the entire spectrum have now been classified.

1. INTRODUCTION

THE classification of the first spark spectrum of thallium has been the subject of papers by Rao, Narayan and Rao,¹ Smith,² McLennan, McLay and Crawford,³ and McLennan and Crawford,⁴ using both their own experimental data and the earlier measurements of Lang⁵ and Carroll.⁶ These investigations established the lowest terms of the various series—with the classification of about 100 lines—but left the upper part of the level diagram, including the interesting $5d^96s^26p$ configuration, incomplete. The lines which would give the clues to the upper levels should fall in the far ultraviolet below 2000Å, in which region thallium has only been studied with the vacuum arc and condensed spark as sources. The most efficient means of producing these lines should be the hollow cathode discharge in He. In this source the Tl atom or ion is excited by collision with a metastable He atom (energy $\sim 160,000 \text{ cm}^{-1}$) or with a He^+ ion (energy $\sim 198,000 \text{ cm}^{-1}$).⁷ Since these energies are just a little less than that required to ionize doubly the Tl atoms ($\sim 213,000 \text{ cm}^{-1}$), very many of the latter will be excited to the upper levels of Tl II. With this in mind we have photographed the hollow cathode spectrum in the entire range from 9250Å to 600Å with the

view of completing the energy level scheme of Tl II.

2. EXPERIMENTAL PROCEDURE

The hollow cathode was filled with He at about one cm pressure which was continuously circulated and purified throughout the exposures. Small pieces of Tl laid inside the cathode immediately melted when the discharge was started. The source of power was a transformer and vacuum tube rectifier set which delivered 1000 volts d.c.—the discharge drawing around 100 ma. For the vacuum lines a normal incidence concave grating vacuum spectrograph⁸ was used. The grating (1 m radius, 15,000 lines/in.) gave a dispersion of about 17Å/mm. For the regions 2100–2500Å the Hilger Quartz E-2, and 2500–4100Å the Hilger Quartz E-1 spectrographs were available. The photographs in the visible and infrared were taken with a spectrograph of the same specifications as the Hilger Glass E-1. In the Schumann region lines of He and of the impurities Ne, Hg, C, and O served as internal wave-length standards. Elsewhere comparison spectra were placed upon the plates: 2100–2500 Åg spark; 2500–5800 Fe arc; and 5800–9250 Ne tube. Besides lines from the above-mentioned atomic impurities there appeared some electronic bands due to the molecules H_2 , CO^+ , OH, and He_2 , for which the hollow cathode seems to be a very powerful source.

Of the thallium lines, in accordance with expectation, the lower series members of Tl I and all of Tl II were very strong; while nothing from

¹ Rao, Narayan and Rao, *Ind. J. Phys.* **2**, 467 (1928).² Smith, *Proc. Nat. Acad. Sci.* **14**, 951 (1928); *Phys. Rev.* **34**, 393 (1929); *Phys. Rev.* **35**, 235 (1930).³ McLennan, McLay and Crawford, *Proc. Roy. Soc. A* **125**, 570 (1929).⁴ McLennan and Crawford, *Proc. Roy. Soc. A* **132**, 10 (1931).⁵ Lang, *Phil. Trans. Roy. Soc.* **224**, 371 (1924).⁶ Carroll, *Phil. Trans. Roy. Soc.* **225**, 357 (1925).⁷ Sawyer, *Phys. Rev.* **36**, 44 (1930).⁸ Sawyer, *J. Opt. Soc. Am.* **15**, 305 (1927).

TABLE I. Energy levels of Tl II.

LEVEL	TERM VALUE (cm^{-1})	LEVEL	TERM VALUE (cm^{-1})	LEVEL	TERM VALUE (cm^{-1})	LEVEL	TERM VALUE (cm^{-1})	LEVEL	TERM VALUE (cm^{-1})
$6s^2 1S_0$	0	$6s7p 1P_1^0$	122,379	$6s7d 3D_2$	138,053	$6s8d 3D_1$	147,602	$6s10p 3P_2^0$	153,530?*
$6s6p 3P_0^0$	49,451	$6p^2 3P_1$	125,338	$6s7d 3D_3$	138,203	$6s8d 3D_2$	147,652	$6s10p 1P_1^0$	153,633?*
$6s6p 3P_1^0$	52,393	$5d^9 6s^2 6p 4s^0$	125,437#	$6s8p 3P_1^0$	139,365*	$6s8d 3D_3$	147,747	$6s11s 3S_1$	155,181*
$6s6p 3P_2^0$	61,725	$5d^9 6s^2 6p 5s^0$	126,204#	$6s8p 3P_2^0$	140,304*	$6s9p 3P_1^0$	148,349*	$6s10d 3D_1$	155,963*
$6s6p 1P_1^0$	75,660	$5d^9 6s^2 6p 6s^0$	128,663*	$6s8p 1P_1^0$	141,000*	$6s8d 1D_2$	148,465	$6s10d 3D_2$	155,982*
$6s7s 3S_1$	105,225	$6p^2 3P_2$	128,817	$6p^2 1D_2$	141,982	$6s9p 3P_2^0$	148,825*	$6s10d 3D_3$	156,018*
$6s7s 1S_0$	107,996	$5d^9 6s^2 6p 7s^0$	129,158*	$5d^9 6s^2 6p 10s^0$	142,781#	$6s9p 1P_1^0$	149,063*	$6s10d 1D_2$	156,177*
$5d^9 6s^2 6p 1s^0$	110,387*	$6s8s 3S_1$	133,568*	$5d^9 6s^2 6p 11s^0$	143,612*	$6s10s 3S_1$	151,568*	$6s11p 1P_1^0$	156,475?*
$6s6d 1D_2$	115,160	$6s8s 1S_0$	134,292*	$5d^9 6s^2 6p 12s^0$	145,092*	$6s7f 3F_2^0$	152,104*	$6s12s 3S_1$	157,481*
$6s6d 3D_1$	116,147	$5d^9 6s^2 6p 8s^0$	134,362*	$6s9s 3S_1$	145,415	$6s7f 3F_3, 4^0$	152,110	$6s11d 3D_2$	158,027?*
$6s6d 3D_2$	116,430	$6s5f 3F_3^0$	136,115	$6s9s 1S_0$	145,591	$6s7f 1F_3^0$	152,140*	$6s11d 3D_3$	158,038?*
$6s6d 3D_3$	116,826	$6s5f 3F_2^0$	136,216	$6s6f 3F_2^0$	146,500	$6s6g$	152,470*	$6s11d 1D_2$	158,136?*
$6p^2 3P_0$	117,408	$6s5f 3F_4^0$	136,230	$6s6f 3F_3^0$	146,523	$6s9d 3D_1$	152,819*		
$6s7p 3P_0^0$	119,361	$6s5f 1F_3^0$	136,263	$6s6f 3F_3^0$	146,534	$6s9d 3D_2$	152,847*		
$6s7p 1P_1^0$	119,576	$6s7d 1D_2$	136,891	$6s6f 1F_3^0$	146,543	$6s9d 3D_3$	152,906*		
$6s7p 3P_2^0$	122,029	$6s7d 3D_1$	137,927	$6s5g$	147,065*	$6s9d 1D_2$	153,200*		

* These terms are newly located from this research.

The terms here named $5d^9 6s^2 6p 4s^0$, $5s^0$, and $10s^0$ were called $3s^0$, $1s^0$, and $2s^0$, respectively, by McLennan and Crawford.

? These high series members are established by only one vacuum line each, and so their term values may be in error by as much as 5 or 6 cm^{-1} . However these approximate positions are justified by the smoothness of the resulting quantum defect curves.

the higher stages of ionization appeared except a few of the most prominent transitions of Tl III and IV, which gave weak lines. Since the record of the 115 previously classified lines is scattered through three papers—those of McLennan, McLay and Crawford,³ Smith,⁹ and McLennan and Crawford⁴—to provide a complete list of Tl II we have included these lines as well as the 160 new ones found by us in Table II. All of the wave-lengths are our own with the exception of those of the three weak lines noted which we did not obtain. Likewise Table I is a complete list of the Tl II energy levels. The discrepancies between the wave numbers of the lines as measured and as computed from these energy levels, given in the $\Delta\nu$ column of Table II, are the best indications of the degree of accuracy of our results—about 6 cm^{-1} in the vacuum region and about 1 cm^{-1} above 2100Å.

3. EXTENSION OF THE SERIES

The normal configuration of Tl II is $5d^{10}6s^2$. Excitation of one of the 6s electrons gives rise to the usual singlet and triplet series of the $6snd$ configurations. Inspection of the energy levels given in Table I shows that all the far ultraviolet lines ($\nu > 115,000 \text{ cm}^{-1}$) must represent transitions ending on the normal state $6s^2 1S_0$ and all the lines in the range $\nu = 115,000$ –50,000 cm^{-1} (except the resonance lines) transitions ending on one of the $6s6p$ levels—otherwise the initial

levels would have to be above the ionization potential. With this clue to the identification of the vacuum lines many higher series members were quickly located. We are greatly indebted to Dr. A. B. McLay, of McMasters University, for the information by personal letter that the level at 145,591 cm^{-1} (called $6s8d 1D_2$ by McLennan and Crawford) is really $6s9s 1S_0$ and that the true position of $6s8d 1D_2$ is 148,465 cm^{-1} —with which we concur. A plot of the quantum defects for each of the series showed that the $3S_1$ and $3D_{1,2,3}$ series are unperturbed, so these were used to determine the ionization potential, i.e., that value of the latter was found by trial which made the ends of the quantum defect curves most nearly horizontal. The best value is $164,765 \pm 5 \text{ cm}^{-1}$.

4. OTHER CONFIGURATIONS AND PERTURBATIONS

In addition to the regular series there are two other configurations which should give rise to observable lines: $5d^{10}6p^2$ and $5d^9 6s^2 6p$. Of the $6p^2$ configuration the three lower levels, $3P_{0,1,2}$ were already known, and the position of a fourth, $\nu = 141,982 \text{ cm}^{-1}$, was given us by Dr. McLay, who considered it to be the $1S_0$ level. However there are three pieces of evidence that this is instead $6p^2 1D_2$. The first is the strong transition to $6s6p 3P_2$ ($\lambda 1246\text{Å}$) which would be forbidden from a $J=0$ level. The second is the perturbation of the $6snd 1D_2$ series shown in Fig. 1 (which is so strong as to depress the lower singlet D 's beneath their triplets). The curve locates the perturbing

⁹ Smith, Phys. Rev. 35, 235 (1930).

TABLE II. Classified lines of Tl II.

INT.	$\lambda(\text{air})$	$\nu(\text{vac})$	TRANSITION	$\Delta\nu$	INT.	$\lambda(\text{air})$	$\nu(\text{vac})$	TRANSITION	$\Delta\nu$
3	9254 A	10,803*	$5f^1F_3 - 5g$	1	0	4462.02	22,404*	$7p^3P_1 - 6p^2^1D_2$	
4	9225	10,837*	$5f^3F_4 - 5g$	2	0	4461.23	22,409*		
2	9216	10,848*	$5f^3F_2 - 5g$	-1	0	4460.70	22,412*	$5d^6s^26p\ 7_2 - 10s^3S_1$	-2
20	9130	10,950*	$5f^3F_3 - 5g$	0	2	4358.82	22,936*	$6d^3D_2 - 8p^3P_1$	1
00	8935	11,189*	$7p^1P_1 - 8s^3S_1$	0	6?	4340.53 H?	23,032}	$7p^1P_1 - 9s^3S_1$	
00	8876	11,263*	$8p^3P_2 - 10s^3S_1$	-1	3	4339.55	23,037}		
1	8673.8	11,526*	$8s^3S_1 - 5d^6s^26p\ 12_2$	2	1	4313.22	23,178*	$5d^6s^26p\ 1_2 - 8s^3S_1$	
10	8664.1	11,539*	$7p^3P_2 - 8s^3S_1$	0	2	4312.37	23,183*		
8	8632.9	11,580*	$7s^1S_0 - 7p^3P_1$	0	10	4306.80	23,213 #	$7p^1P_1 - 9s^1S_0$	1
0	8528.7	11,722*	$5d^6s^26p\ 5_1 - 7d^3D_1$	-1	0	4292.72	23,289 #	$6p^2^3P_2 - 7f^3F_2$	2
8	8445.8	11,837*	$6d^3D_2 - 5d^6s^26p\ 6_3$	0	1	4291.72	23,294	$6p^2^3P_2 - 7f^3F_3, 4$	-1
2	8436.9	11,849*	$5d^6s^26p\ 5_1 - 7d^3D_2$	0	4d	4286.51	23,322*	$6p^2^3P_2 - 7f^1F_3$	-1
4	8389.9	11,916*	$7p^1P_1 - 8s^1S_0$	3	20	4274.98	23,385 #	$7p^3P_2 - 9s^3S_1$	
1	8194.0	12,201*	$8p^1P_1 - 9d^1D_2$	1	3	4274.24	23,389 #		
0	7934.0	12,601*	$8p^3P_2 - 9d^3D_3$	-1	2	4258.07	23,489*	$6d^3D_3 - 8p^3P_2$	0
1	7683.6	13,011*	$6d^3D_1 - 5d^6s^26p\ 7_2$	0	1	4256.82	23,485*	$6p^2^3P_1 - 9p^3P_3$	
2	7144.9	13,992*	$7p^3P_1 - 8s^3S_1$	0	1	4256.09	23,489*		
00	7110.2	14,059*	$8s^1S_0 - 9p^3P_1$	2	3	4224.31	23,666*		
4	7073.9	14,133}	$7s^3S_1 - 7p^3P_0$	0	8	4223.05	23,673*	$6d^3D_2 - 8p^3P_2$	0
2	7070.8	14,139}			0	4187.41	23,874*		
00	7035.6	14,209*	$7p^3P_0 - 8s^3S_1$	2	3	4177.46	23,931*	$5d^6s^26p\ 7_2 - 7s^3S_1$	
10	6966.5	14,351 #	$7s^3S_1 - 7p^3P_1$	0	1	4176.75	23,935*		
4	6950.5	14,384 #	$7s^1S_0 - 7p^1P_1$	1	0	4069.05	24,569*	$6d^3D_2 - 8p^1P_1$	-1
2	6888.8	14,512 #	$7p^1P_1 - 7d^1D_2$	0	3	3955.65	25,273 #	$7p^1P_1 - 8d^3D_3$	0
0	6727.2(c)	14,861	$7p^3P_2 - 7d^1D_3$	0	3	3909.5(c)	25,571 #	$7p^3P_2 - 8d^3D_2$	
0	6587.40	15,176*	$8d^1D_2 - 10d^1D_2$	-1	1	3901.53	25,624 #	$7p^3P_2 - 8d^3D_3$	0
1	6555.70	15,250*	$7p^1D_2 - 7f^1F_3$	1	10	3887.15	25,718 #	$6d^1D_2 - 8p^1P_1$	-2
2	6552.63	15,257*	$8s^3S_1 - 9p^3P_2$	0	2	3869.15	25,838 #	$7p^3P_1 - 9s^3S_1$	0
0	6452.05	15,495*	$8s^3S_1 - 9p^1P_1$	-2	6			$6d^3D_3 - 5d^6s^26p\ 10_3$	-1
3	6430.45	15,547 #	$7p^1P_1 - 7d^3D_1$	0	2	3851.87	25,954 #	$7p^3P_1 - 9s^1S_0$	-1
10	6378.32	15,674 #	$7p^1P_1 - 7d^3D_2$	0	2	3842.93	26,014 #	$7p^3P_1 - 9s^3S_1$	1
2	6289.74	15,895}	$7p^3P_2 - 7d^3D_1$	0	4	3836.95	26,055 #	$7p^3P_0 - 9s^3S_1$	1
1	6287.55	15,900*			10	3832.30	26,087*	$7p^1P_1 - 8d^1D_2$	1
8d	6239.03	16,024 #	$7p^3P_2 - 7d^3D_3$	0	8	3793.95	26,350	$6d^3D_2 - 5d^6s^26p\ 10_3$	-1
10	6179.98	16,177 #	$7p^3P_2 - 7d^3D_3$	0	2	3791.56	26,367*	$7s^1S_0 - 5d^6s^26p\ 8_1$	1
1	6170.03	16,203*			2	3619.49	27,621	$6d^1D_2 - 5d^6s^26p\ 10_3$	0
4	6167.38	16,210*	$5f^1F_3 - 6g$	2	3	3593.61	27,819*	$5d^6s^26p\ 1_2 - 7d^3D_3$	3
1	6156.17	16,239*			5	3567.67	28,022 #	$7p^3P_1 - 8d^3D_1$	
4	6154.03	16,245*	$5f^3F_4 - 6g$	0	4	3566.84	28,028 #		
2	6151.02	16,253*	$5d^6s^26p\ 7_2 - 9s^3S_1$	0	9	3560.68	28,077 #	$7p^3P_1 - 8d^3D_2$	1
1	6149.01	16,258*	$5f^3F_2 - 6g$	-1	8	3540.08	28,240 #	$7p^3P_0 - 8d^3D_3$	-1
2	6113.87	16,352*	$5f^3F_3 - 6g$	2	2	3536.70	28,267*	$6d^3D_3 - 5d^6s^26p\ 12_2$	1
4	6111.50	16,358*			1	3513.80	28,451*	$6d^1D_2 - 5d^6s^26p\ 11_1$	-1
25	5949.48	16,804 #	$7s^3S_1 - 7p^3P_2$	0	0	3487.81	28,663*	$6d^3D_2 - 5d^6s^26p\ 12_2$	1
3	5828.59	17,152 #	$7s^3S_1 - 7p^1P_1$	0	6d	3460.48	28,890*	$7p^3P_1 - 8d^1D_2$	2
2	5826.58	17,158 #			3	3453.83	28,945*	$6d^3D_1 - 5d^6s^26p\ 12_2$	0
3	5774.00	17,314 #	$7p^3P_1 - 7d^1D_2$	2	2	3384.47	29,538*	$7p^3P_2 - 10s^3S_1$	-1
2	5772.71	17,318			6	3381.80	29,562 #	$6p^1P_1 - 7s^3S_1$	
4d	5643.00	17,716 #	$6p^2^3P_2 - 6f^3F_3$	-1	8	3381.00	29,569 #		
4d	5640.06	17,725 #	$6p^2^3P_2 - 6f^1F_3$	-1	15	3369.15	29,673 #	$6d^3D_3 - 6f^3F_4$	-1
2	5581.76	17,911*			2	3365.48	29,705 #	$6d^3D_3 - 6f^3F_3$	-3
4	5490.47	18,208	$7s^1S_0 - 5d^6s^26p\ 5_1$	0	2	3364.05	29,718	$6d^3D_3 - 6f^1F_3$	1
4	5448.77	18,347 #	$7p^3P_1 - 7d^3D_1$	4	4	3339.91	29,932*	$6d^1D_2 - 5d^6s^26p\ 12_2$	0
2	5446.85	18,354 #			8	3322.25	30,092 #	$6d^3D_2 - 6f^3F_2$	-1
10	5410.97	18,476 #	$7p^3P_1 - 7d^3D_2$	12	12	3321.04	30,102 #	$6d^3D_2 - 6f^3F_3$	-2
7	5409.92	18,479			12	3319.91	30,113 #	$6d^3D_2 - 6f^1F_3$	0
15d	5384.85	18,566 #	$7p^3P_0 - 7d^3D_1$	0	15	3291.01	30,377 #	$6d^3D_1 - 6f^3F_2$	1
1	5206.29	19,202*	$6d^1D_2 - 5d^6s^26p\ 8_1$	0	4	3243.68	30,820*	$7p^1P_1 - 9d^1D_2$	-1
6	5183.10	19,288}	$6d^3D_3 - 5f^3F_3$	15	4	3237.96	30,875*	$7p^3P_2 - 9d^3D_3$	-2
6	5181.95	19,292}			15	3187.74	31,361*	$6d^1D_2 - 6f^3F_2$	-2
0	5156.40	19,388	$6d^3D_3 - 5f^3F_2$	-2	15	3186.56	31,373 #	$6d^1D_2 - 6f^3F_3$	-1
25	5152.14	19,404 #	$6d^3D_3 - 5f^3F_4$	0	15	3185.51	31,383 #	$6d^1D_2 - 6f^1F_3$	0
1	5143.81	19,435 #	$6d^3D_3 - 5f^1F_3$	-2	20	3091.56	32,337 #	$6p^1P_1 - 7s^1S_0$	1
1	5099.71	19,604*	$7p^1P_1 - 6p^2^1D_2$	1	5	3029.01	33,004*	$7s^1S_0 - 8p^1P_1$	0
25	5078.54	19,685 #	$6d^3D_2 - 5f^3F_3$	0	0	3015.52	33,152*	$7p^3P_2 - 11s^3S_1$	0
3	5053.14	19,784 #	$6d^3D_2 - 5f^3F_2$	0	00	3007.05	33,245*	$7p^3P_1 - 9d^3D_1$	2
3	5052.35	19,787 #			3	3004.71	33,271*	$7p^3P_1 - 9d^3P_2$	0
2	5040.55	19,833 #	$6d^3D_2 - 5f^1F_3$	0	2	2987.95	33,458*	$7p^3P_0 - 9d^3D_1$	0
15	4981.35	20,069 #	$6d^3D_1 - 5f^3F_2$	0	00	2973.30	33,623*	$7p^3P_1 - 9d^1D_2$	-1
2	4946.63	20,210 #			0	2957.85	33,799*	$7p^1P_0 - 10d^1D_2$	1
1	4945.53	20,215 #	$7s^3S_1 - 5d^6s^26p\ 4_2$	4	4	2948.73	33,903*	$6d^1D_2 - 9p^1P_1$	0
0	4938.20	20,245*	$6p^2^3P_2 - 9p^1P_1$	-1	0	2941.28	33,989*	$7p^3P_2 - 10d^3D_3$	0
4	4770.70	20,955 #	$6d^1D_2 - 5f^1F_3$	0	2	2928.21	34,141*	$7s^3S_1 - 8p^3P_1$	1
2	4765.75	20,977}	$7s^3S_1 - 5d^6s^26p\ 5_1$	0	0	2854.25	35,025*	$5d^6s^26p\ 1_2 - 9s^3S_1$	
1	4764.58	20,982}			1	2853.86	35,030*		
0	4748.05	21,055	$6d^1D_2 - 5f^3F_2$	-1	10	2849.80	35,081*	$7s^3S_1 - 8p^3P_2$	-2
20	4737.05	21,104 #	$6d^1D_2 - 5f^1F_3$	1	2	2833.31	35,284	$6d^3D_3 - 7f^3F_3, 4$	0
0	4661.23	21,448}	$5d^6s^26p\ 5_1 - 8d^3D_2$	0	0	2807.75	35,605*	$7p^3P_1 - 11s^3S_1$	0
0	4660.75	21,450}			2	2806.80	35,617*	$7s^1S_0 - 5d^6s^26p\ 11_1$	1
3	4500.03	22,216*	$5d^6s^26p\ 4_2 - 8d^3D_2$	1	3	2801.81	35,681	$6d^3D_2 - 7f^3F_3, 4$	1
8	4490.77	22,262*	$5d^6s^26p\ 5_1 - 8d^1D_2$	1	1	2794.59	35,773*	$7s^3S_1 - 8p^1P_1$	-2
2	4481.46	22,308*			3	2780.25	35,957*	$6d^3D_1 - 7f^3F_2$	0
2	4480.80	22,311*	$5d^6s^26p\ 4_2 - 8d^3D_3$	0	00	2746.01	36,406*	$7p^3P_1 - 10d^3D_2$	0

* These lines are newly located and classified.

Hyperfine structure, here unresolved, has been observed in these lines by previous investigators.

(a) This line coincides with $6p_{1/2} - 13d$ of Tl I.(b) This line coincides with the third order of $\lambda 670.87$.

(c) These wave-lengths are taken from previous lists, and included for the sake of completeness, but they were not observed by us.

d, An unresolved doublet.

R, ν Reversed lines.In the above term designations the "6s" has been omitted from the symbols for the $6sml$ configurations.

TABLE II.—Continued.

INT.	$\lambda(\text{air})$	$\nu(\text{vac})$	TRANSITION	$\Delta\nu$	INT.	$\lambda(\text{vac})$	$\nu(\text{vac})$	TRANSITION	$\Delta\nu$
00	2731.29	36,602*	$7p\ ^3P_0 - 10d\ ^3D_1$	0	2	1312.42	76,195*	$6p\ ^3P_2 - 7d\ ^3D_1$	-7
3	2705.55(c)	36,950	$6d\ ^1D_2 - 7f\ ^3F_{3,4}$		8R	1310.20	76,324	$6p\ ^3P_2 - 7d\ ^3D_2$	-4
2	2703.36	36,980*	$6d\ ^1D_2 - 7f\ ^1F_3$	0	4R	1308.50	76,423	$6p\ ^3P_1 - 6p^2\ ^3P_2$	-1
2	2682.61	37,266*	$5d^2\ ^6S^2\ ^6p\ 1_2 - 8d\ ^3D_2$	1	15R	1307.50	76,482	$6p\ ^3P_2 - 7d\ ^3D_3$	4
4	2676.03	37,358*			4r	1289.58	77,545*	$6p\ ^1P_1 - 9d\ ^1D_2$	5
4	2675.76	37,362*	$5d^2\ ^6S^2\ ^6p\ 1_2 - 8d\ ^3D_3$		2	1254.34	79,723*		
2	2604.32	38,386*			5R	1246.00	80,257*	$6p\ ^3P_2 - 6p^2\ ^1D_2$	0
1	2604.01	38,391*	$7s\ ^3S_1 - 5d^2\ ^6S^2\ ^6p\ 11_1$		3	1242.00	80,515*	$6p\ ^1P_1 - 10d\ ^1D_2$	-2
20	2530.86	39,500#	$6p\ ^1P_1 - 6d\ ^1D_2$	0	8	1231.81	81,181*	$6p\ ^3P_1 - 8s\ ^3S_1$	6
4	2507.70	39,865*			2	1221.02	81,899*	$6p\ ^3P_1 - 8s\ ^1S_0$	0
3	2507.39	39,870*	$7s\ ^3S_1 - 5d^2\ ^6S^2\ ^6p\ 12_2$		1	1212.47	82,476*	$6p\ ^1P_1 - 11d\ ^1D_2$	0
4?	2477.40(a)	40,353*	$7s\ ^1S_0 - 9p\ ^3P_1$	0	12R	1194.84	83,693*	$6p\ ^3P_2 - 9s\ ^3S_1$	3
6	2469.03	40,489#	$6p\ ^1P_1 - 6d\ ^3D_1$	2	3r	1188.83	84,116*	$6p\ ^3P_0 - 8s\ ^3S_1$	-1
8	2451.83	40,773#	$6p\ ^1P_1 - 6d\ ^3D_2$	3	10R	1183.41	84,501	$6p\ ^3P_1 - 7d\ ^1D_2$	3
2	2434.28	41,067*	$7s\ ^1S_0 - 9p\ ^1P_1$	0	5R	1169.17	85,531	$6p\ ^3P_1 - 7d\ ^3D_1$	-3
2	2403.57	41,592*			10R	1167.43	85,658	$6p\ ^3P_1 - 7d\ ^3D_2$	-2
0	2394.71	41,746	$6p\ ^1P_1 - 6p^2\ ^3P_0$	-2	2	1164.50	85,874*	$6p\ ^3P_2 - 8d\ ^3D_1$	-3
0	2318.20	43,124*	$7s\ ^3S_1 - 9p\ ^3P_1$	0	4R	1163.80	85,925*	$6p\ ^3P_2 - 8d\ ^3D_2$	-2
30	2298.04	43,502#	$6p\ ^3P_2 - 7s\ ^3S_1$	2	15R	1162.55	86,018	$6p\ ^3P_2 - 8d\ ^3D_3$	-4
4	2292.97	43,598*	$7s\ ^3S_1 - 9p\ ^3P_2$	-2	3	1152.90	86,738*	$6p\ ^3P_2 - 8d\ ^1D_2$	-2
					10R	1130.17	88,482*	$6p\ ^3P_0 - 7d\ ^3D_1$	6
					4	1113.06	89,850*	$6p\ ^3P_2 - 10s\ ^1S_1$	7
					2	1097.43	91,130*	$6p\ ^3P_2 - 9d\ ^3D_2$	8
					3r	1096.73	91,188*	$6p\ ^3P_2 - 9d\ ^3D_3$	7
					1	1093.25	91,470*	$6p\ ^3P_2 - 9d\ ^1D_2$	-5
					5R	1074.97	93,026*	$6p\ ^3P_1 - 9s\ ^3S_1$	4
					3	1072.99	93,198*	$6p\ ^3P_1 - 9s\ ^1S_0$	0
					0	1070.08	93,451*	$6p\ ^3P_2 - 11s\ ^3S_1$	-5
					2	1060.93	94,257*	$6p\ ^3P_2 - 10d\ ^3D_2$	2
					3	1060.53	94,292*	$6p\ ^3P_2 - 10d\ ^3D_3$	-1
					8R	1050.30	95,211*	$6p\ ^3P_1 - 8d\ ^3D_1$	2
					10R	1049.73	95,263*	$6p\ ^3P_1 - 8d\ ^3D_2$	2
					2	1044.37	95,752*	$6p\ ^3P_2 - 12s\ ^3S_1$	-4
					3r	1042.00	95,969*	$6p\ ^3P_0 - 9s\ ^3S_1$	5
					3r	1040.88	96,072*	$6p\ ^3P_1 - 8d\ ^1D_2$	10
					2	1038.28	96,313*	$6p\ ^3P_2 - 11d\ ^3D_3$	0
					8R	1018.85	98,150	$6p\ ^3P_0 - 8d\ ^3D_1$	-1
					0	1008.33	99,174*	$6p\ ^3P_1 - 10s\ ^3S_1$	-1
					4r	995.54	100,448*	$6p\ ^3P_1 - 9d\ ^3D_2$	-6
					1	991.99	100,808*	$6p\ ^3P_1 - 9d\ ^1D_2$	1
					3	979.30	102,114*	$6p\ ^3P_0 - 10s\ ^3S_1$	-3
					4	967.42	103,368*	$6p\ ^3P_0 - 9d\ ^3D_1$	0
					4	965.41	103,583*	$6p\ ^3P_1 - 10d\ ^3D_2$	-6
					1	963.60	103,778*	$6p\ ^3P_1 - 10d\ ^1D_2$	-6
					1	951.55	105,092*	$6p\ ^3P_1 - 12s\ ^3S_1$	4
					2	946.70	105,630*	$6p\ ^3P_1 - 11d\ ^3D_2$	0
					2	945.79	105,732*	$6p\ ^3P_0 - 11s\ ^3S_1$	2
					2	938.82	106,517*	$6p\ ^3P_0 - 10d\ ^3D_1$	5
					5R	836.34	119,569*	$6s^2\ ^1S_0 - 7p\ ^3P_1$	-7
					10R	817.18	122,372	$6s^2\ ^1S_0 - 7p\ ^1P_1$	-7
					4r	792.40	126,199	$6s^2\ ^1S_0 - 5d^2\ ^6S^2\ ^6p\ 5_1$	-5
					2	744.27	134,360*	$6s^2\ ^1S_0 - 5d^2\ ^6S^2\ ^6p\ 8_1$	-2
					4	717.55	139,363*	$6s^2\ ^1S_0 - 8p\ ^3P_1$	-2
					5R	709.23	140,998*	$6s^2\ ^1S_0 - 8p\ ^1P_1$	-2
					15R	696.30	143,616*	$6s^2\ ^1S_0 - 5d^2\ ^6S^2\ ^6p\ 11_1$	-2
					4	674.10	148,346*	$6s^2\ ^1S_0 - 9p\ ^3P_1$	-3
					5R	670.87	149,060*	$6s^2\ ^1S_0 - 9p\ ^1P_1$	-3
					3	650.90	153,633*	$6s^2\ ^1S_0 - 10p\ ^1P_1$	0
					1	639.08	156,475*	$6s^2\ ^1S_0 - 11p\ ^1P_1$	0

term, which can only be $6p^2\ ^1D_2$, in the region of the new level in question. Thirdly, the curve for the $6sns\ ^1S_0$ series (Fig. 2), which can only be perturbed by $6p^2\ ^1S_0$, points to the location of the latter somewhere above $6s9s\ ^1S_0$ —probably around $151,000\text{ cm}^{-1}$. For these reasons we have called the level at $141,982\text{ cm}^{-1}$ $6p^2\ ^1D_2$. (However, since the perturbation is so strong, the “ $6s7d\ ^1D_2$ ” and “ $6p^2\ ^1D_2$ ” levels must each have both sd and p^2 properties, so that these two names might very well be interchanged, and have really become meaningless.) The $6p^2\ ^1S_0$ level could not be located.

To the three previously known levels of $5d^2\ ^6S^2\ ^6p$ we have added six, leaving from the predicted

twelve levels only three missing. As these three, with $J=0, 3$, and 4 , should probably give rise each to only one observable line they could not be reliably established. The distribution of the levels found indicates near- jj coupling and is very similar to that of the d^2p levels of the Pt I sequence recently studied by Mack and Fromer,¹⁰ and Goble,¹¹ as shown by the comparison with Au II in Fig. 3. However, differences between these two configurations should arise not only from differences in coupling between Tl II and Au II, but from displacements of some of the thallium levels due to interactions with the odd

¹⁰ Mack and Fromer, Phys. Rev. **48**, 357 (1935).

¹¹ Goble, Phys. Rev. **48**, 346 (1935).

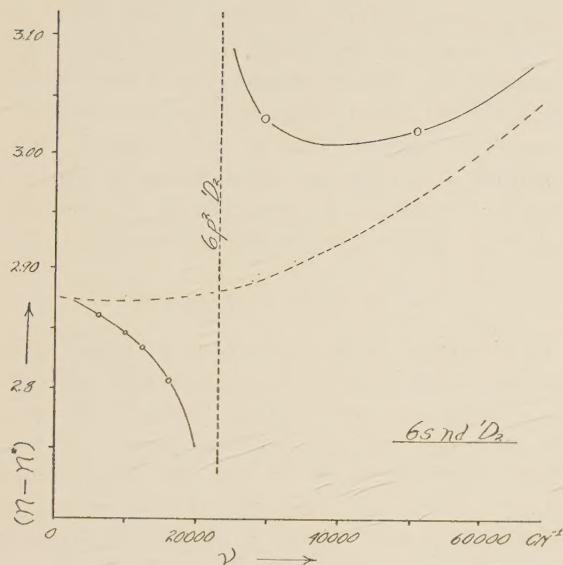


FIG. 1. Perturbation of the singlet D series by $6p^2\ ^1D_2$.

sp and sf series. The effect of the perturbations upon these series is very marked. Fig. 2 shows the disturbance of the 1P_1 series by 8_1 , (the reaction

upon the latter level being evident in Fig. 3). The $7p\ ^3P_1$ and the $7p\ ^3P_0$ are probably displaced downwards slightly by 5_1 and the missing $J=0$ level. The repulsion due to the levels 10_3 and 12_2 , lying between $5f$ and $6f$, displaces $5f\ ^3F_3$ downwards and $6f\ ^3F_{2,3}$ upwards—leading to the partial inversions apparent in these configurations.

5. HYPERFINE STRUCTURE

The dispersion of our plates did not permit accurate measurements of the hyperfine structure. However, McLennan and Crawford's⁴ h.f.s. term separations were confirmed to the extent that those of our new lines whose structure was large enough to be observed fitted into the system as transitions to just those levels known to have the largest separations. In the case of the $6f$ multiplet the large h.f.s. explains the nearly equal intensities of the lines from $6f\ ^3F_3$ and $6f\ ^1F_3$ to $6d\ ^3\ ^1D_2$. These levels, $6d\ ^3\ ^1F_3$, are so near together that their h.f.s. components can interact, since their F values are the same,

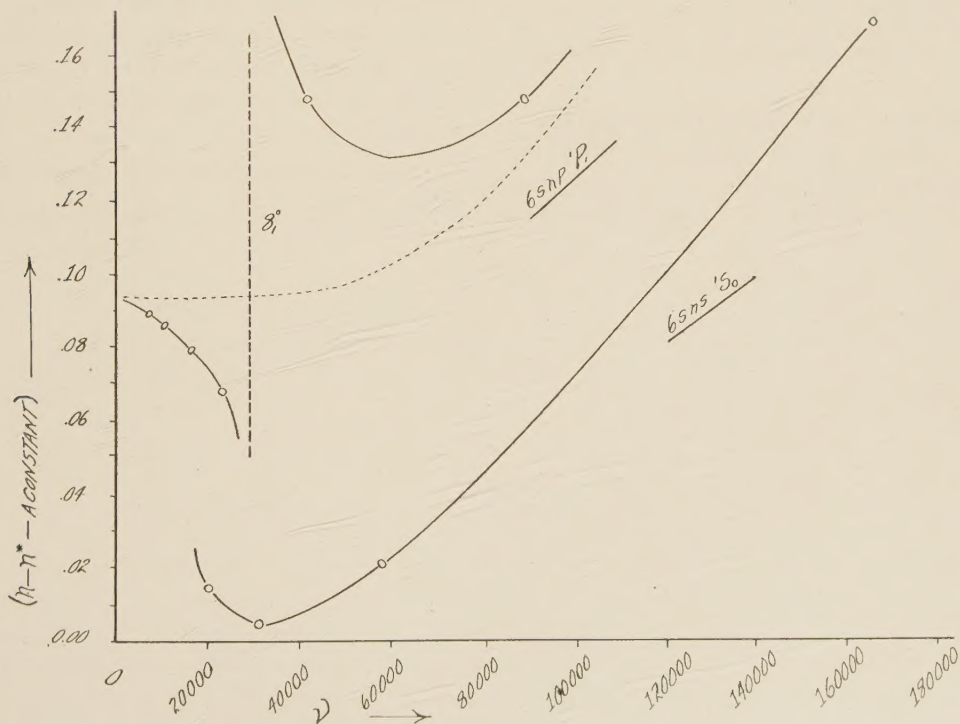


FIG. 2. Perturbation of the singlet P series by $5d^9 6s^2 6p\ 8_1$, and of the singlet S series by the unlocated $6p^2\ ^1S_0$. A constant has been subtracted from the quantum defects (4.20 for the S , and 3.63 for the P series) in order to bring both curves into the same figure.

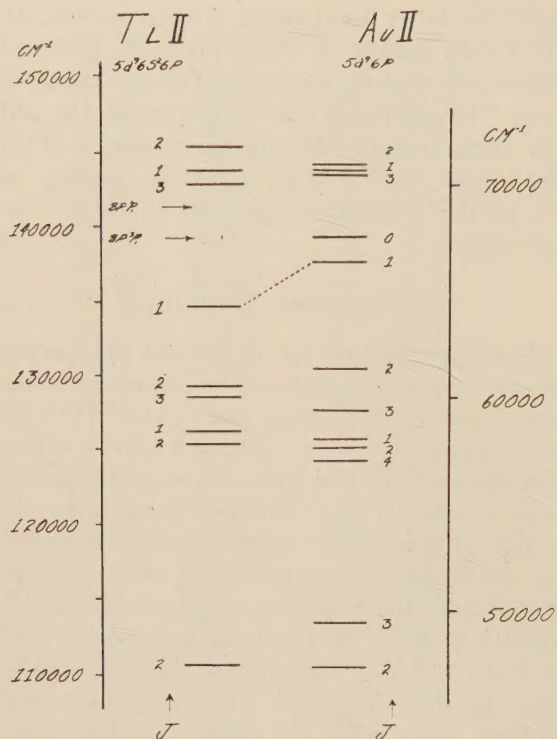


FIG. 3. A comparison of the configurations $5d^6s^26p$ of Tl II and $5d^66p$ of Au II. The arrows show the positions of $6s8p^3.1P_1$ which probably cause the large shift in the middle $J=1$ level. Three of the Tl levels are still unlocated.

causing the two terms to share their properties—each being partly 1F and partly 3F . With the newly found $6g$ configuration the ratio of h.f.s. to multiplet separation is even larger. The

$5f-6g$ transitions indicate the presence of two $6g$ levels, separated by about 6 cm^{-1} . These are probably the two hyperfine structure components, the multiplet structure being too small to observe. A similar case of h.f.s. larger than multiplet structure has been found in Al II.¹² Structure could not be observed in $5g$ since the transitions fall in a region of low dispersion.

6. REMAINING LINES

In the entire spectrum there now remain only five unclassified lines of intensity greater than 1, these being also included in Table II. Besides these five our plates showed one important line ($2210.75\text{\AA}$; $45,219\text{ cm}^{-1}$; int. 10) which must belong to the arc spectrum. There seems no possible place for it in the Tl II system; furthermore it has been previously observed as reversed in the arc by Kayser and Runge.¹³ An arc line of this frequency, and reversed, can only be a transition ending on the ground state. The initial level is thus established as a new even term in Tl I (with $J=\frac{1}{2}$ or $1\frac{1}{2}$), at an absolute value of 4045 cm^{-1} , and probably belongs to the $6s6p^2$ configuration expected in that region.

We wish to express our appreciation to Dr. S. A. Goudsmit for his interest in the work and to Dr. McLay for the location of the levels previously mentioned.

¹² Paschen, Preuss. Akad. Wiss. Berlin, Ber. 32, 502 (1932).

¹³ Kayser, *Handbuch der Spektroskopie*, Vol. 6, p. 709.

